



# Effect of ceria on the structure and catalytic activity of $V_2O_5/TiO_2-ZrO_2$ for oxidehydrogenation of ethylbenzene to styrene utilizing $CO_2$ as soft oxidant

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## ABSTRACT

The present study was undertaken to investigate the influence of ceria on the physicochemical and catalytic properties of  $V_2O_5/TiO_2-ZrO_2$  for oxidative dehydrogenation of ethylbenzene to styrene utilizing  $CO_2$  as a soft oxidant. Monolayer equivalents of ceria, vanadia and ceria–vanadia combination over  $TiO_2-ZrO_2$  (TZ) support were impregnated by a coprecipitation and wet impregnation methods. Synthesized catalysts were characterized by using X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, temperature programmed reduction, transmission electron microscopy and BET surface area methods. The XRD profiles of 550 °C calcined samples revealed amorphous nature of the materials. Upon increasing calcination temperature to 750 °C, in addition to  $ZrTiO_4$  peaks, few other lines due to  $ZrV_2O_7$  and  $CeVO_4$  were observed. The XPS V 2p results revealed the existence of  $V^{4+}$  and  $V^{5+}$  species at 550 and 750 °C calcinations temperatures, respectively. TEM analysis suggested the presence of nanosized (<7 nm) particles with narrow range distribution. Raman measurements confirmed the formation  $ZrTiO_4$  under high temperature treatments. TPR measurements suggested a facile reduction of  $CeO_2-V_2O_5/TZ$  sample. Among various samples evaluated, the  $CeO_2-V_2O_5/TZ$  sample exhibited highest conversion and nearly 100% product selectivity. In particular, the addition of ceria to  $V_2O_5/TZ$  suppressed the coke deposition and allowed a stable and high catalytic activity.

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## 1. Introduction

As industrial demand for styrene grows, its production via dehydrogenation (DH) of ethylbenzene (EB) is receiving greater importance. DH of styrene is highly endothermic reaction and requires high reaction temperatures (around 600–700 °C) and low ethylbenzene pressures [1–3]. Presently, more than 90% of styrene is produced based on catalytic dehydrogenation of EB. As a consequence of high reaction temperature and excess superheated steam, the conventional process suffers from poor economy and rapid catalyst deactivation owing to coke formation. Since the process is equilibrium-limited and energy intensive, there is a great interest for the development of an alternative methodology. Recently, oxidative dehydrogenation (ODH) process has been realized as one of the most elegant routes to produce styrene. Moreover, the ODH process has been widely investigated by variety of oxidizing agents such as dry air,  $O_2$ ,  $N_2O$ ,  $SO_2$  and so on [4–6]. It has been realized very recently that  $CO_2$  can act as a soft

oxidant as well as diluent [2]. There are a number of additional benefits for utilizing  $CO_2$  unlike the other oxidants. In particular, (i) there is no loss of latent heat for  $CO_2$  because  $CO_2$  stays in the gaseous form throughout the reaction [7]. (ii)  $CO_2$  can decrease the partial pressure of reactants more effectively than steam and it has the highest heat capacity among various typical gases [8,9]. (iii) It also minimizes the significant quantities of valuable hydrocarbons leading to the generation of unwanted carbon oxides. (iv) Further, in the presence of  $CO_2$ , coupling between reverse water–gas shift ( $CO_2 + H_2 \leftrightarrow CO + H_2O$ ) and EBDH reaction becomes more favorable [9–11]. Therefore, utilization of  $CO_2$  as a soft oxidant would be highly desirable for efficient conversion of EB to styrene.

Recently, several attempts were made in the literature for exploitation of ODH of EB by means of  $CO_2$  as soft oxidant [9–20]. In this direction, a variety of active components like Fe-, Cr-, V-, Sn- and La-oxides [9–15] supported over different materials like carbonaceous materials, hydrotalcite-type compounds, zeolites,  $Al_2O_3$ ,  $Ga_2O_3$ ,  $ZrO_2$  and  $TiO_2$  [16–20] have been investigated. However, our recent studies revealed that titania–zirconia mixed oxides exhibit excellent catalytic activity and selectivity for the title reaction [12–14,20]. The significant features of  $TiO_2-ZrO_2$  mixed oxides include a high specific surface area, profound acid–base and

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redox properties together, high thermal stability and strong mechanical strength. In general, the ODH reaction using  $\text{CO}_2$  as soft oxidant is believed to result in the formation of more carbonaceous deposits resulting in the fast deactivation of the catalysts. Therefore, there is an urge to design better catalyst systems, which can overcome the deactivation disadvantage. Recently, Murugan and Ramaswamy [21] reported a low temperature ODH of EB over ceria containing catalysts and noticed that ceria-based materials follow the Mars-van Krevelen mechanism and exhibit promising catalytic properties. Reddy and co-workers [22–26] also investigated the ceria-based materials for ODH and DH reactions, and uncovered that ceria containing materials suppress catalyst deactivation by preventing coke formation during the reaction. It is a known fact that  $\text{CeO}_2$ -based mixed oxides are effective catalysts for oxidation of different hydrocarbons and for the removal of total organic carbon from polluted waters from different sources. It has also been established that the presence of  $\text{CeO}_2$  promotes various catalytic reactions such as  $\text{CO}_2$  activation [27], CO oxidation [26,28] and CO/NO removal [29]. Therefore, ceria and ceria containing materials are receiving a great deal of attention due to the unique ability of ceria to shift easily between reduced and oxidized states ( $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$ ) and to accommodate variable levels of bulk and surface oxygen vacancies [21–23,30]. These favorable characteristics make them as suitable for use as supports as well as catalysts in the processes wherein reaction conditions fluctuate between oxidizing and reducing environments. However, bulk cerium and vanadium oxides are susceptible to sintering leading to fall in the surface area and decrease in the stability of the structure during high-temperature applications. The rapid deactivation promotes the non-selective oxidations [31]. Hence, the combination of vanadia (known for its redox properties) and ceria (known for its oxygen storage and release functions) is expected to provide better catalytic systems.

In view of the problem of global warming and energy crisis, the utilization of  $\text{CO}_2$  for a reaction like ODH of EB could be considered as a promising approach. Therefore, the present investigation was undertaken against the aforesaid background. In this study a  $\text{CeO}_2$  promoted  $\text{V}_2\text{O}_5/\text{TiO}_2\text{--ZrO}_2$  catalyst along with  $\text{CeO}_2/\text{TiO}_2\text{--ZrO}_2$ ,  $\text{V}_2\text{O}_5/\text{TiO}_2\text{--ZrO}_2$  and  $\text{TiO}_2\text{--ZrO}_2$  were synthesized and evaluated for the ODH of EB using  $\text{CO}_2$  as the soft oxidant. To determine the physicochemical properties of various samples synthesized, different characterization techniques namely, BET surface area (SA), pore size distribution (PSD), X-ray diffraction (XRD), Raman spectroscopy (RS), temperature programmed reduction (TPR) of  $\text{H}_2$ , transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were employed. To know the deactivation phenomenon of catalysts, the spent catalysts were also subjected to XRD and XPS analysis.

## 2. Experimental

### 2.1. Catalyst preparation

The  $\text{TiO}_2\text{--ZrO}_2$  (1:1 mole ratio) mixed oxide was synthesized by a coprecipitation method by hydrolysis with ammonium hydroxide. In a typical experiment, the required quantities of zirconyl(IV) nitrate hydrate (Acros Organics, USA) and titanium(IV) chloride (Yakuri Pure Chemicals, Japan) were dissolved separately in deionised water and mixed together. To this mixture solution, dilute aqueous ammonia was used as precipitating agent and the resultant precipitates were aged hydrothermally for 12 h at  $100^\circ\text{C}$  [25,32]. The obtained precipitates were filtered off and washed several times with deionised water until free from anion impurities. The obtained cake was oven dried at  $120^\circ\text{C}$  for 12 h and finally calcined at  $550^\circ\text{C}$  for 6 h. On the calcined  $\text{TiO}_2\text{--ZrO}_2$  (TZ) mixed oxide support, a monolayer equivalent of  $\text{V}_2\text{O}_5$

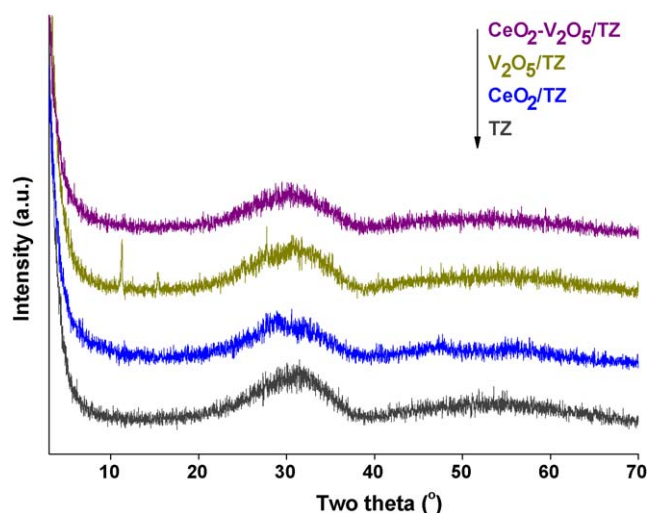
(15 wt.%),  $\text{CeO}_2$  (15 wt.%) and  $\text{CeO}_2\text{--V}_2\text{O}_5$  (7.5 wt.% + 7.5 wt.%) were deposited by adopting a standard wet impregnation method. To carry out this, the desired quantities of ammonium metavanadate (Aldrich) and ceric ammonium nitrate (TCI, Japan) were dissolved in deionised water to which the finely powdered support was added with continuous stirring. The excess water was evaporated on a water-bath under vigorous stirring. The resulting material was once again oven dried at  $120^\circ\text{C}$  for 12 h and subsequently calcined at  $550^\circ\text{C}$  for 6 h in air atmosphere. Some portions of the finished samples were again heated at  $750^\circ\text{C}$  for 6 h to investigate their thermal stability.

### 2.2. Catalyst characterization

Powder X-ray diffraction patterns were recorded on a Rigaku Multiflex instrument using nickel-filtered  $\text{Cu K}\alpha$  (0.15418 nm) radiation source and a scintillation counter detector. The intensity data were collected over a  $2\theta$  range of  $2\text{--}80^\circ$  with a  $0.02^\circ$  step size and using a counting time of 1 s per point. Crystalline phases were identified by comparison with the reference data from International Center for Diffraction Data (ICDD) files. The BET surface area and BJH pore size distribution measurements were made by  $\text{N}_2$  adsorption/desorption at liquid-nitrogen temperature using a Micromeritics ASAP 2020 instrument. Before analysis, samples were evacuated for 3–4 h at  $250^\circ\text{C}$  in the degassing port of the instrument. Raman spectra were recorded on a LabRam HR800UV Raman spectrometer (Horiba Jobin-Yvon) equipped with a confocal microscope and liquid-nitrogen cooled CCD detector at ambient temperature and pressure. The emission line at 325 nm from He–Cd laser (Melles Griot Laser) was focused on the sample under microscope. The time of acquisition was adjusted according to the intensity of Raman scattering. The XPS measurements were made on a KRATOS (ESCA AXIS 165) spectrometer by using  $\text{Mg K}\alpha$  (1253.6 eV) radiation as the excitation source. Charging of catalyst samples was corrected by setting the binding energy of adventitious carbon (C 1s) at 284.6 eV. The TEM images were obtained on a JEM-2010 (JEOL) instrument equipped with a slow-scan CCD camera and at an accelerating voltage of 400 kV. Samples were sonically dispersed in ethanol and deposited on a carbon coated copper grid before examination. The TPR measurements were made on a Pulse Chemisorb 2705 (Micromeritics, USA) instrument. Before the TPR measurement, the sample was preconditioned by passing dry air (20 ml/min) at  $400^\circ\text{C}$  for 2 h and later the temperature was brought down to  $100^\circ\text{C}$ . The TPR was run from 100 to  $700^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  in 5%  $\text{H}_2$  in argon gas mixture.

### 2.3. Catalyst activity

The catalytic activity for vapor phase ODH of EB was investigated in a down flow fixed-bed stainless steel microreactor. For each run,  $\sim 1.0$  g of sample was loaded in the reactor. The reactor was heated to  $600^\circ\text{C}$  at a rate of  $2^\circ\text{C}/\text{min}$  in the flow of He (20 ml/min) and kept at this temperature for 2 h and He was replaced with  $\text{CO}_2$  gas. The catalyst pretreatment was continued at  $600^\circ\text{C}$  for 30 min with  $\text{CO}_2$  (20 ml/min) before conducting the reaction. The EB was introduced into the preheating zone of the reactor through a liquid feed pump with a constant feed rate of 9.8 mmol/h. Gaseous and liquid products were analyzed simultaneously by an on-line gas chromatograph (Younlin Instrument, Acme 6000 Series, Korea) equipped with TCD and FID. For analysis of liquid products, HP-innowax column (30 m long, 0.32 mm i.d. and 0.25  $\mu\text{m}$  film thickness) was employed and for the gaseous products Porapak N 80/100 column (6 ft  $\times$  1/8 in.) was used. The main liquid products analyzed were styrene, benzene, toluene, benzaldehyde, and acetophenone; and the gaseous products were hydrogen, methane, carbon monoxide and carbon dioxide.

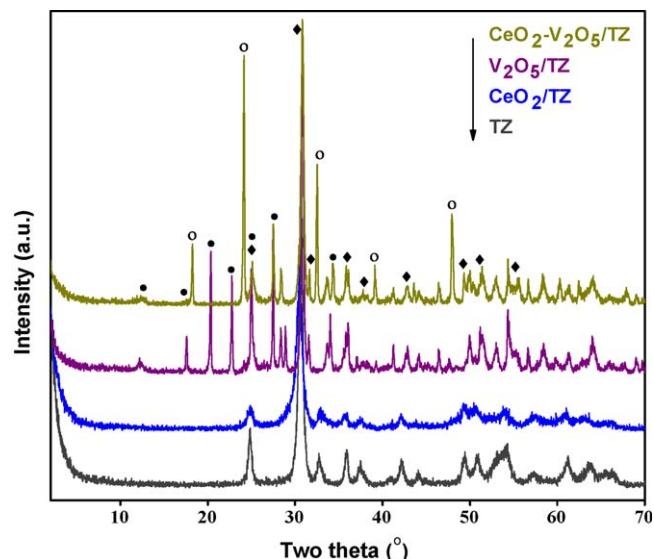


**Fig. 1.** X-ray powder diffractions of  $\text{TiO}_2\text{-ZrO}_2$  (TZ),  $\text{CeO}_2/\text{TiO}_2\text{-ZrO}_2$ ,  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ , and  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  samples calcined at 550 °C.

### 3. Result and discussion

#### 3.1. XRD and XPS

The powder XRD profiles of various samples calcined at 550 °C are presented in Fig. 1. As can be noted from Fig. 1, no independent diffraction lines due to crystalline  $\text{TiO}_2$  (anatase or rutile) and  $\text{ZrO}_2$  (monoclinic, tetragonal or cubic) were observed. The X-ray diffraction profiles showed two broad peaks revealing the amorphous or poorly crystalline nature of catalysts. The XRD profiles of  $\text{V}_2\text{O}_5$  and  $\text{CeO}_2$  containing samples revealed that the impregnated oxides are in a highly dispersed form. The XRD profiles of promoted samples further suggest no substantial increase in the crystallinity of the support after impregnation with  $\text{V}_2\text{O}_5$  and  $\text{CeO}_2$ . However, in the present study the quantity of vanadia and ceria selected is lower than the theoretical monolayer capacity of the TZ support, based on its specific surface area [32]. To know the bulk composition of the impregnated materials and to understand their thermal stability at high temperatures, these samples were subjected to 750 °C calcination and the corresponding XRD profiles are depicted in Fig. 2. All samples exhibited characteristic diffraction lines due to  $\text{ZrTiO}_4$  compound [20,22–25]. In case of  $\text{CeO}_2/\text{TZ}$  sample, there are no characteristic lines due to ceria indicating that cerium dioxide is in well dispersed state over the TZ support. Whereas  $\text{V}_2\text{O}_5$  containing samples exhibited supplementary peaks pertaining to  $\text{ZrV}_2\text{O}_7$  crystalline compound in addition to the  $\text{ZrTiO}_4$  phase. In case of  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TZ}$  sample, additional lines due to  $\text{CeVO}_4$  are also noted. The crystallite size measurements were carried out by using the intense  $\text{ZrTiO}_4$  line ( $2\theta = 30^\circ$ ) of the 750 °C calcined



**Fig. 2.** X-ray powder diffractions of  $\text{TiO}_2\text{-ZrO}_2$  (TZ),  $\text{CeO}_2/\text{TiO}_2\text{-ZrO}_2$ ,  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ , and  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  samples calcined at 750 °C: (♦) lines due to  $\text{ZrTiO}_4$ ; (●) lines due to  $\text{ZrV}_2\text{O}_7$ ; (○) lines due to  $\text{CeVO}_4$ .

samples and observed that the addition of ceria to  $\text{V}_2\text{O}_5/\text{TZ}$  decreases the crystallite size by ~5 nm. The pure support (TZ) and  $\text{CeO}_2/\text{TZ}$  sample exhibited crystallite sizes of 17 and 12.7 nm, respectively. As revealed by XRD measurements (Figs. 1 and 2), the impregnated vanadia and ceria are in a highly dispersed state on the TZ support at 550 °C. Upon increase of calcination temperature from 550 to 750 °C, binary compounds such as  $\text{ZrV}_2\text{O}_7$  and  $\text{CeVO}_4$  in addition to  $\text{ZrTiO}_4$  were observed.

To investigate the surface composition of various catalysts, XPS measurements were performed and the corresponding binding energy values of the elements O 1s, Ce 3d, Zr 3d, Ti 2p, and V 2p are listed in Table 1. The O 1s core level XPS profiles of various samples subjected to 550 and 750 °C thermal treatments are shown in Fig. 3A and B, respectively. As can be observed from these figures, all the profiles consist of broad peaks ranging from 528 to 534 eV, which could be assigned to the lattice oxygen associated with the metal oxides [23,26]. The O 1s profiles are more complicated due to the overlapping contribution of oxygen from titania, zirconia, ceria, vanadia and from their mixed oxide compounds. With increase of calcination temperature a small increase in the binding energy values (Table 1) and sharpening of the peaks (Fig. 3B) are observed which could be due to better crystallization of the individual and/or mixed oxides inline with XRD analysis. Of course, it is well-known that the XPS peak intensity depends on both ion density and its chemical environment. The oxygen ion density in various samples is expected to be same. Therefore, the decrease in the peak

**Table 1**

BET surface area, pore volume and binding energy values of  $\text{TiO}_2\text{-ZrO}_2$  (TZ),  $\text{CeO}_2/\text{TiO}_2\text{-ZrO}_2$ ,  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  and  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  samples calcined at 550 and 750 °C.

Sample	Surface area (m <sup>2</sup> /g)	Pore volume (ml/g)	Binding energy (eV)				
			O 1s	Ce 3d <sub>5/2</sub>	Zr 3d <sub>5/2</sub>	Ti 2p <sub>3/2</sub>	V 2p <sub>3/2</sub>
Calcined at 550 °C							
TZ	207	0.65	530.0	–	182.1	458.5	–
V <sub>2</sub> O <sub>5</sub> /TZ	175	0.46	530.0	–	182.0	458.5	516.3
CeO <sub>2</sub> /TZ	189	0.51	529.9	882.4	182.0	458.4	–
CeO <sub>2</sub> –V <sub>2</sub> O <sub>5</sub> /TZ	170	0.45	530.0	882.1	182.1	458.5	516.7
Calcined at 750 °C							
TZ	112	–	530.5	–	182.7	459.1	–
V <sub>2</sub> O <sub>5</sub> /TZ	82	–	530.3	–	182.5	458.8	517.4
CeO <sub>2</sub> /TZ	96	–	530.1	882.8	182.2	458.7	–
CeO <sub>2</sub> –V <sub>2</sub> O <sub>5</sub> /TZ	88	–	530.2	883.2	182.4	458.9	517.4



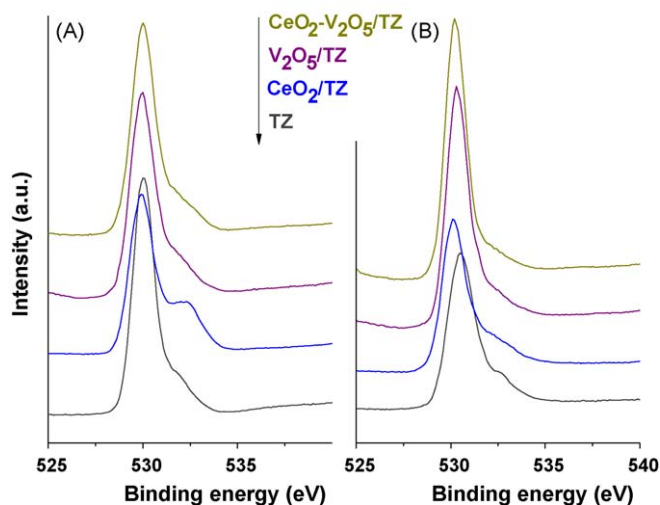


Fig. 3. O 1s XPS profile of TiO<sub>2</sub>-ZrO<sub>2</sub> (TZ), CeO<sub>2</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub>, and CeO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> samples calcined at 550 °C (A) and 750 °C (B).

intensity can be attributed to different chemical environments [23,32].

V 2p photoelectron peaks of the V<sub>2</sub>O<sub>5</sub>/TZ and CeO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>/TZ catalysts calcined at 550 and 750 °C are shown in Fig. 4. The 550 °C calcined samples exhibited broad V 2p<sub>3/2</sub> lines at ~516.3 eV; it is probably due to the presence of V<sup>4+</sup> species over the surface. However, with increase of calcination temperature from 550 to 750 °C, the binding energy of V 2p<sub>3/2</sub> increased from 516.3 to 517.4 eV (Table 1), an indication of increase in the oxidation state of vanadium that could be due to the formation of crystalline zirconium bivanadate. Vanadia in the 4+ oxidation state is stabilized on the amorphous TZ mixed oxide support when calcined at 550 °C [33]. As the calcination temperature increased, the formation of crystalline ZrTiO<sub>4</sub> and ZrV<sub>2</sub>O<sub>7</sub> occurred, thereby decreasing the proportion of amorphous material. Thus, the newly formed crystalline ZrV<sub>2</sub>O<sub>7</sub> compound stabilizes in the 5+ state of vanadium. From these data it is also clear that the binding energy of the V 2p<sub>3/2</sub> peak is more sensitive to the nature of the carrier material [34,35]. The intensity of V 2p peak decreased with an increase in the calcination temperature for V<sub>2</sub>O<sub>5</sub>/TZ system,

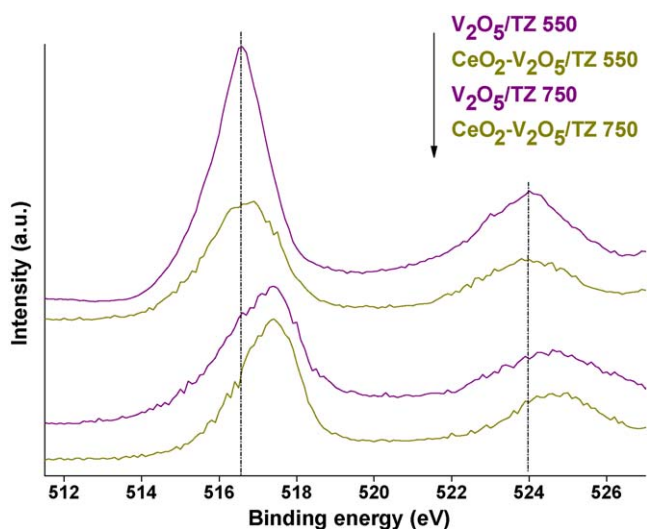


Fig. 4. V 2p core level XPS profile of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> and CeO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> samples calcined at 550 and 750 °C.

whereas no such change was observed in the case of CeO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>/TZ catalyst. This observation suggests the addition of ceria has stabilized the vanadia and suppressed the formation of specific compounds. The same observation was also illustrated from the XRD analysis. Table 1 discloses the core level electron binding energies of Zr 3d and Ti 2p for various samples calcined at two different temperatures. The photoelectron signals of Ti 2p are observed at 458.5 and 464.4 eV corresponding to the spin orbital multiplets of Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>, respectively [36]. Both Zr 3d and Ti 3d binding energies represent the presence of 4+ oxidation state for Zr and Ti. Interestingly, the binding energy values of Zr and Ti core levels increased with increase in the calcination temperature. This could be due to better crystallization of the materials and formation of new phases like ZrTiO<sub>4</sub> and ZrVO<sub>7</sub> [36]. Recently, Victor and Krupanidhi [37] also reported the O 1s, Zr 3d and Ti 2p BE values for ZrTiO<sub>4</sub> at 530.27, 182.24 and 458.66 eV, respectively which are close to the present XPS data. The present results are thus corroborating very well with the earlier findings.

The Ce 3d XPS profiles of CeO<sub>2</sub>/TZ and CeO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>/TZ samples calcined at 550 and 750 °C are shown in Fig. 5. As can be noted from the figure, the Ce 3d profiles are more complicated due to mixing of Ce 4f levels with O 2p states. The notation of the Ce 3d peaks in the present study are envisaged as elucidated in the literature [23,38]. Two sets of spin-orbit multiplets, corresponding to the 3d<sub>5/2</sub> and 3d<sub>3/2</sub> contributions are labeled as *u* and *v*, respectively. The *u'''*/*v'''* doublet is due to the primary photoemission from Ce<sup>4+</sup>. The *u*/*v* and *u''*/*v''* doublets are shake-down features resulting from the transfer of one or two electrons from a filled O 2p orbital to an empty Ce 4f orbital. The *u*<sub>0</sub>, *v*<sub>0</sub> and *u'*/*v'* doublet are due to photoemission from Ce<sup>3+</sup> cations. As previously pointed out, the XPS spectrum of CeO<sub>2</sub>/TZ sample calcined at 550 °C exhibits peaks due to the presence of both Ce<sup>4+</sup> and Ce<sup>3+</sup>, thus implying that cerium is present at the surface in both 4+ and 3+ oxidation states [23,26,33]. On high temperature calcination as well as addition of vanadia the binding energy values of Ce 3d shifted slightly to higher side, suggesting small shift in the binding energies that could be due to different metal ions environment near the cerium sites.

### 3.2. BET surface area and pore volume

The specific surface areas of various samples calcined at 550 and 750 °C are presented in Table 1. As can be noted from Table 1,

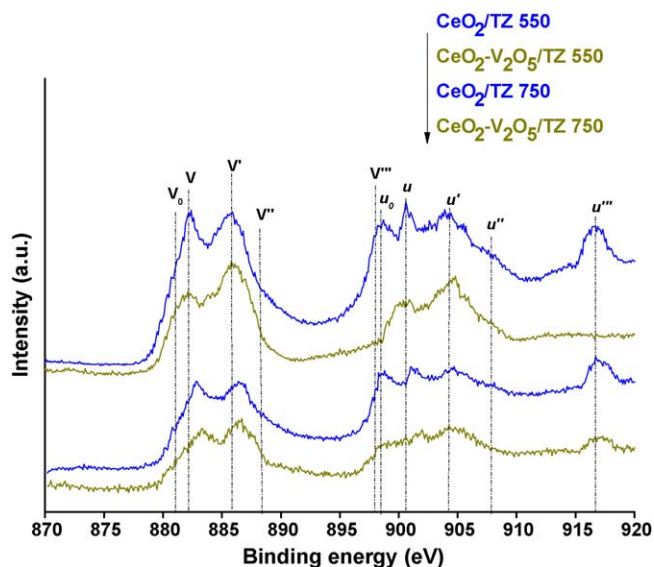


Fig. 5. Ce 3d XPS profile of CeO<sub>2</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> and CeO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> samples calcined at 550 and 750 °C.

the synthesized TZ mixed oxide exhibited a high specific surface area of 207 m<sup>2</sup>/g. Interestingly, it is higher than its individual component oxides, namely TiO<sub>2</sub> (15 m<sup>2</sup>/g) and ZrO<sub>2</sub> (25 m<sup>2</sup>/g) [13,14]. The high specific surface area of the titania–zirconia mixed oxide is due to the amorphous nature as well as the porosity of the material. The porosity of the synthesized materials is ascribed to the preparation method adopted and the precursors used in the present investigation. With increase in the calcination temperature there is a sudden drop in the surface area that could be attributed to the formation of nonporous TiZrO<sub>4</sub>. Of course, there is slight decrease in the surface area and pore volume in the case of vanadia and ceria impregnated samples (Table 1). The decrease in the specific surface area after impregnating with V<sub>2</sub>O<sub>5</sub> or CeO<sub>2</sub> is due to various factors, mainly, penetration of the deposited active oxides into the pores of the support thereby narrowing its pore diameter and blocking some of the micropores, and solid-state reaction between the dispersed active oxide and the supporting material [23,26].

### 3.3. Raman spectroscopy and TEM

The existence of TiZrO<sub>4</sub> is further confirmed by Raman spectra as shown in Fig. 6. The spectrum of TZ sample calcined at 550 °C mainly contained broad bands ranging from 200 to 370 cm<sup>−1</sup>, 420 to 475 cm<sup>−1</sup> and 680 to 890 cm<sup>−1</sup>, which should be assigned as an amorphous material [37,39]. Thermal treatment of TZ in air atmosphere at 750 °C leads to drastic changes in the Raman spectrum. The position and shape of these bands are different from either TiO<sub>2</sub> or ZrO<sub>2</sub>. As reported in the literature, the classification of each active mode of titania–zirconia mixed oxide by Raman spectrum is very difficult due to the structural conformation of this oxide [40]. However, a comparison with literature results of the number and position of peaks of the Raman spectra (Fig. 6) show a minimal discrepancy. Some of the fluctuations are related to different syntheses methodologies, in particular due to the difference in the heat treatments [39,40]. The spectrum exhibited

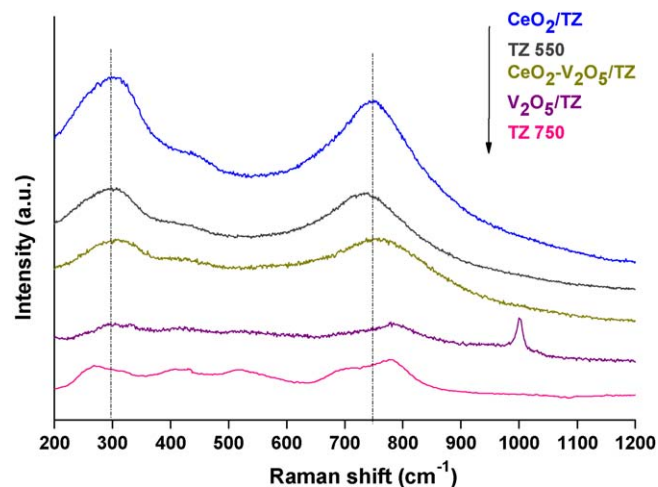


Fig. 6. Raman spectra of TiO<sub>2</sub>–ZrO<sub>2</sub> (TZ 550), CeO<sub>2</sub>/TiO<sub>2</sub>–ZrO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>–ZrO<sub>2</sub>, and CeO<sub>2</sub>–V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>–ZrO<sub>2</sub> samples calcined at 550 °C and TiO<sub>2</sub>–ZrO<sub>2</sub> (TZ 750) sample calcined at 750 °C.

bands (263, 337, 478, 635, and 784 cm<sup>−1</sup>) at low frequency range. Based on the above arguments, the observed bands could be assigned to the existence of TiZrO<sub>4</sub> composition. Thus Raman results indicate the presence of zirconia in titania with the formation of TiZrO<sub>4</sub> that retard the phase transformation and thereby improving the textual properties at high temperatures. The V<sub>2</sub>O<sub>5</sub>/TZ sample exhibited mainly two broad bands in the high frequency region from 700 to 1100 cm<sup>−1</sup>, centered at about 775 and 1002 cm<sup>−1</sup>, and these bands can be assigned to the formation of ZrV<sub>2</sub>O<sub>7</sub> compound. Present results are in well agreement with the previous reports on V<sub>2</sub>O<sub>5</sub>/ZrO<sub>2</sub> systems, where the formation of ZrV<sub>2</sub>O<sub>7</sub> was observed at higher calcination temperatures [41]. In the case of V<sub>2</sub>O<sub>5</sub>/TZ sample, in addition to the broad bands of ZrTiO<sub>4</sub> and ZrV<sub>2</sub>O<sub>7</sub>, a few extra broad signals due to the dispersed

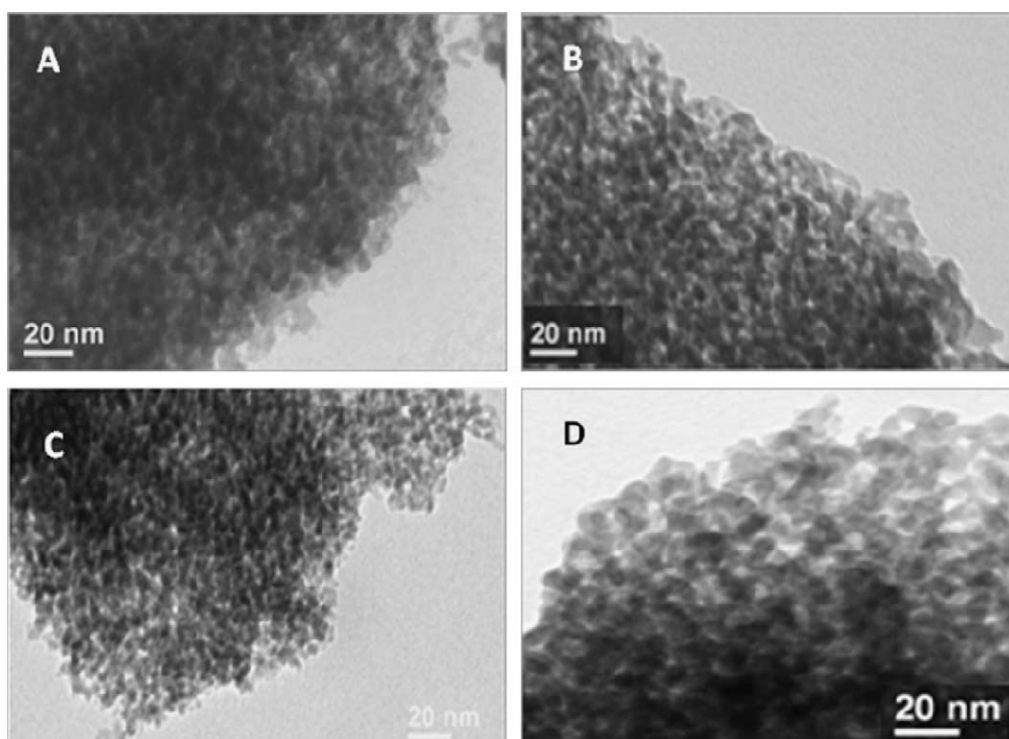


Fig. 7. TEM images of CeO<sub>2</sub>–V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>–ZrO<sub>2</sub> (A), V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>–ZrO<sub>2</sub> (B), CeO<sub>2</sub>/TiO<sub>2</sub>–ZrO<sub>2</sub> (C) and TiO<sub>2</sub>–ZrO<sub>2</sub> (D) samples calcined at 550 °C.

vanadium oxide have been noted. In the case of  $\text{CeO}_2/\text{TZ}$  and  $\text{CeO}_2\text{--V}_2\text{O}_5/\text{TZ}$  samples, only the broad background bands due to an amorphous  $\text{ZrTiO}_4$  compound could be noted. Pure  $\text{CeO}_2$  exhibits a band at  $460\text{ cm}^{-1}$  and smaller bands at  $239$  and  $590\text{ cm}^{-1}$ , respectively [42]. On the whole, the Raman measurements supported the observations made from XRD and XPS techniques.

To know the textural properties of various samples calcined at  $550^\circ\text{C}$ , TEM analysis was performed and the representative micrographs are presented in Fig. 7. As shown in Fig. 7, the TEM results are supporting the information obtained from other techniques. The  $\text{TiO}_2\text{--ZrO}_2$  support is composed of snowflake type networks with nanometer-sized particles (Fig. 7D). This morphology generally leads to a loose structure with high specific surface area and pore volume, which has been confirmed by  $\text{N}_2$  adsorption measurements. In all the images, small, well faceted particles with narrow range distribution were clearly visible. The impregnated active components (ceria and vanadia) seems to be well distributed on the support, i.e. homogeneous in nature. It is a known fact that control of microstructures is an important factor for the improvement of catalytic activity. Moreover, the addition of vanadium and cerium oxides had strong influence on the particle size of the  $\text{TiO}_2\text{--ZrO}_2$  support as revealed by the TEM images. Further, TEM image of  $\text{CeO}_2\text{--V}_2\text{O}_5/\text{TZ}$  sample revealed the combination features of  $\text{CeO}_2/\text{TZ}$  and  $\text{V}_2\text{O}_5/\text{TZ}$  samples, respectively. In particular, the vanadium containing samples exhibited enhanced grain size compared to the other samples. As mentioned earlier, the accelerated particle size increase is due to better crystallization of  $\text{TiO}_2$  and  $\text{ZrO}_2$ , which are influenced by vanadium oxide [20,22].

### 3.4. Temperature programming reduction

To assess the reducibility of the dispersed compounds and interaction between support and the active components, temperature programming reduction was performed. The  $\text{H}_2$ -TPR profiles of various samples calcined at  $550^\circ\text{C}$  are displayed in Fig. 8. TPR patterns revealed interesting information about the relative reducibility of the mixed oxides. The TZ support exhibited a sharp high temperature reduction peak at  $\sim 748^\circ\text{C}$  and another broad peak at  $\sim 870^\circ\text{C}$ . This clearly shows that the TZ mixed oxide is quite stable due to the formation of an amorphous or poorly crystalline  $\text{ZrTiO}_4$  compound [12–14,36]. There is a small combination negative peak observed at around  $720^\circ\text{C}$  which might be due to release of substrate by the support or from the formation of new phase as TPR temperature was higher than

the original calcination temperature [43]. In general, pure  $\text{V}_2\text{O}_5$  is reduced by hydrogen in four characteristic steps [44]. According to Bosch et al. [44] the four steps of the reduction process of vanadia was described as  $\text{V}_2\text{O}_5 \rightarrow \text{V}_6\text{O}_{13} \rightarrow \text{VO}_2 \rightarrow \text{V}_n\text{O}_{2n-1} \rightarrow \text{V}_2\text{O}_3$  ( $4 < n < 8$ ). The reduction of pure  $\text{V}_2\text{O}_5$  was observed only at temperatures above  $700^\circ\text{C}$ . However, the TPR profiles of the vanadia containing catalysts exhibited peaks at lower temperatures (Fig. 8) compared to the pure  $\text{V}_2\text{O}_5$ . Moreover, the reduction temperatures of all the peaks were decreased due to the influence of the TZ support. Normally, the crystallite size combined with crystal orientation play a major role in the reduction behavior of various oxides. As envisaged in the literature, the unsupported  $\text{V}_2\text{O}_5$  has a random orientation of various crystallographic planes exposed to the reduction gas mixture, whereas the supported  $\text{V}_2\text{O}_5$  displays a preferred orientation and exhibits better reducibility. Accordingly, the dispersed vanadia over the TZ support is expected to reduce at lower temperatures than the bulk  $\text{V}_2\text{O}_5$ . In the case of  $\text{CeO}_2$  containing sample two low intense hydrogen consumption bands were observed at  $\sim 475$  and  $780^\circ\text{C}$  due to the reduction of surface oxygen and bulk reduction of  $\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3$ , respectively. Interestingly, the  $\text{CeO}_2\text{--V}_2\text{O}_5/\text{TZ}$  sample exhibited a broad and well defined reduction peak at  $598^\circ\text{C}$  and another weak and broad peak at  $780^\circ\text{C}$ . This profile is different from the reduction profiles of  $\text{V}_2\text{O}_5/\text{TZ}$  and  $\text{CeO}_2/\text{TZ}$  samples. The intense peak is primarily due to the reduction of the dispersed ceria–vanadia mixed oxide phase over the TZ support, which is formed owing to solid-state reactions between them. It can be noted that the addition of ceria to  $\text{V}_2\text{O}_5/\text{TZ}$  sample promoted the reducibility as well as the dispersion of vanadium oxide species. The TPR peaks were not well resolved under the experimental conditions employed in the present study. Therefore, quantification of the data was not attempted.

### 3.5. Activity studies

The activity studies for oxidehydrogenation of EB were carried out in the vapor phase at normal atmospheric pressure employing  $\text{CO}_2$  as a mild oxidant. Due to the endothermic nature of the reaction, for all the catalytic systems an increasing trend of EB conversion was observed with increasing reaction temperature. The promoted samples exhibited better activity compared to the parent TZ support. Our earlier study revealed that TZ mixed oxide exhibits exceptionally better conversion and product selectivity than its individual component oxides under identical reaction conditions [12–14]. The observed high activity and selectivity of the TZ was proved to be due to the formation of an amorphous compound, enhancement in the specific surface area, and an increase in the number and strength of acid–base sites. As reported in the literature, it has also been observed that initially with time-on-stream there is an enhancement in the activity due to the formation of a thin layer of carbonaceous deposits, which promote the ODH activity [45]. Hence, for better comparison the catalytic data obtained after 3–4 h has been considered. Among various samples evaluated, the  $\text{CeO}_2\text{--V}_2\text{O}_5/\text{TZ}$  sample exhibited highest conversion (56%) and product selectivity (98%).

A fast catalyst deactivation is often encountered on most of the catalytic systems in the dehydrogenation of EB due to coke formation. Therefore, time-on-stream studies were performed to understand the behavior of catalysts. A series of time-on-stream studies were carried out at a constant temperature and optimum space velocity and accounted in Fig. 9. A fast deactivation of  $\text{V}_2\text{O}_5/\text{TZ}$  sample was clearly seen from the figure and the faster deactivation is owing to heavy coke deposition over the surface of the catalyst as established by an increase in the weight of catalyst after the reaction [45]. Further, the activities of other catalysts (except  $\text{V}_2\text{O}_5/\text{TZ}$ ) were found to improve with time in the first few hours of the reaction and there is no drastic fall in the activity

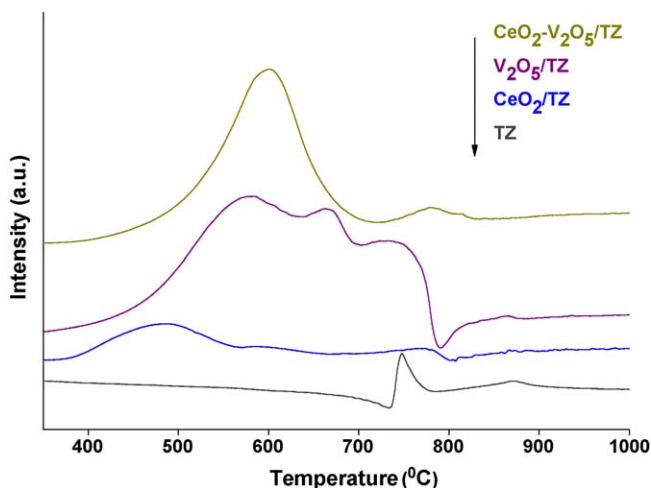
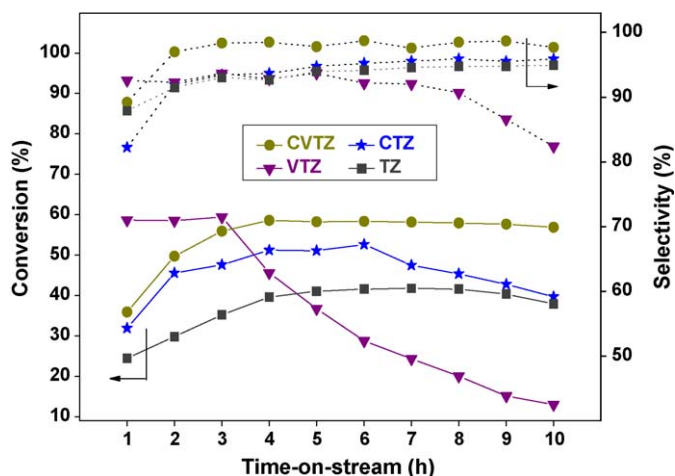


Fig. 8. The TPR ( $\text{H}_2$ ) profiles of  $\text{TiO}_2\text{--ZrO}_2$  (TZ),  $\text{CeO}_2/\text{TiO}_2\text{--ZrO}_2$ ,  $\text{V}_2\text{O}_5/\text{TiO}_2\text{--ZrO}_2$ , and  $\text{CeO}_2\text{--V}_2\text{O}_5/\text{TiO}_2\text{--ZrO}_2$  samples calcined at  $550^\circ\text{C}$ .

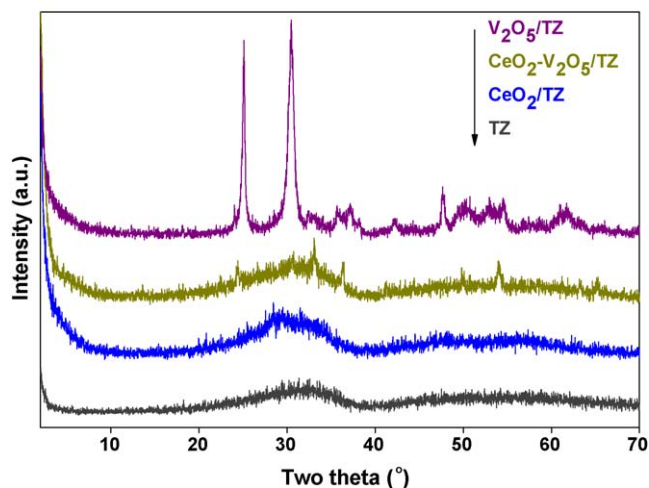




**Fig. 9.** Variation of catalytic activity and selectivity with time-on-stream over  $\text{TiO}_2\text{-ZrO}_2$  (TZ),  $\text{CeO}_2/\text{TiO}_2\text{-ZrO}_2$  (CTZ),  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  (VTZ) and  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  (CVTZ) samples. Reaction conditions:  $T = 600^\circ\text{C}$ ,  $P = 1$  atm,  $W/F = 16.73$  g cat h/mol,  $\text{CO}_2/\text{EB} = 5.1$  (molar ratio).

beyond 10 h of time-on-stream experiments. Interestingly, ceria-vanadia combination sample showed increased conversion in the first 4 h then remained constant up to 10 h with higher conversion and almost 100% selectivity. Therefore, the addition of ceria to vanadia improved the catalytic activity in terms of conversion and selectivity by preventing excess coke deposition over the catalyst surface. The stable activity of ceria-based catalysts is mainly due to facile oxygen transport from the bulk of  $\text{CeO}_2$  [21,25]. The remarkable ability of  $\text{CeO}_2$  in  $\text{V}_2\text{O}_5/\text{TZ}$  catalysts to obtain a high and stable activity is clearly apparent from the present study. To gain information about the deactivation phenomenon of these catalysts, the spent catalysts (after time-on-stream) were subjected to XRD and XPS analysis.

Fig. 10 shows the X-ray powder diffraction profiles of used catalysts. As can be noted from the figure, except for  $\text{V}_2\text{O}_5/\text{TZ}$  sample there no significant change in the XRD patterns of used and fresh (Fig. 1) samples. Hence, after the time-on-stream measurements also the crystallinity and bulk composition of the catalysts remained unaltered. Whereas,  $\text{V}_2\text{O}_5/\text{TZ}$  sample showed lines due to the crystalline  $\text{ZrTiO}_4$  as observed for  $750^\circ\text{C}$  calcined sample. These observations clearly signify the role of ceria in preventing the catalyst deactivation and maintaining a high and stable

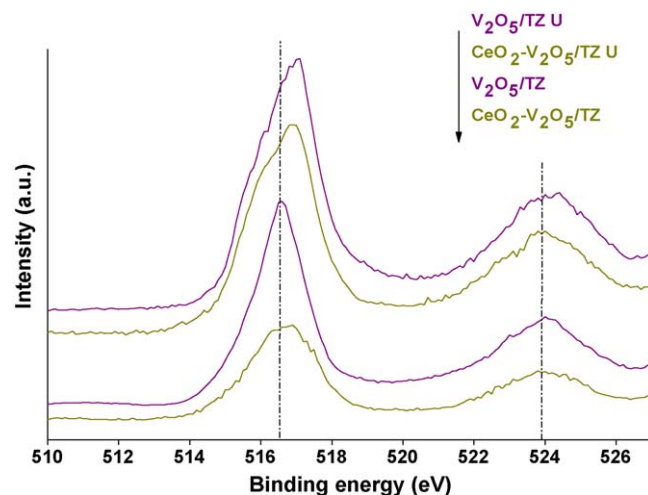


**Fig. 10.** X-ray powder diffractions of used  $\text{TiO}_2\text{-ZrO}_2$  (TZ),  $\text{CeO}_2/\text{TiO}_2\text{-ZrO}_2$ ,  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ , and  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  samples (after catalytic activity measurements).

**Table 2**

Binding energy value of used  $\text{TiO}_2\text{-ZrO}_2$  (TZ),  $\text{CeO}_2/\text{TiO}_2\text{-ZrO}_2$ ,  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  and  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  samples (after time-on-stream measurements).

Sample	Binding energy (eV)				
	O 1s	Ce 3d <sub>5/2</sub>	Zr 3d <sub>5/2</sub>	Ti 2p <sub>3/2</sub>	V 2p <sub>3/2</sub>
TZ	529.8	–	182.0	458.5	–
$\text{V}_2\text{O}_5/\text{TZ}$	529.7	–	181.9	458.2	517.1
$\text{CeO}_2/\text{TZ}$	529.8	882.2	181.9	458.5	–
$\text{CeO}_2\text{-V}_2\text{O}_5/\text{TZ}$	529.8	881.7	182.0	458.3	516.7



**Fig. 11.** V 2p core level XPS profiles of fresh and used (U),  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  and  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  samples.

activity. Table 2 presents the electron binding energy values of various used samples. As presented in Table 2, the binding energy values of O 1s, Zr 3d, and Ti 2p are similar for used and fresh samples. These results once again support the XRD findings, i.e. there is no specific change in the Zr and Ti composition under reaction conditions. However, V 2p of  $\text{V}_2\text{O}_5/\text{TZ}$  shows a decrease in the binding energy value (Table 2) suggesting changes in the chemical environment of vanadium after activity measurements. As depicted in Fig. 11, the used vanadia containing samples show an increase in the intensity as well as broadening of the XPS signals. Moreover, there is a clear shift in the V 2p<sub>3/2</sub> by 0.8 eV, which emphasize the formation of  $\text{ZrV}_2\text{O}_7$  type mixed oxide over the surface under activity measurements. In conclusion, the catalytic activity results from the present study suggest that vanadia and ceria impregnated titania-zirconia mixed oxides exhibit a stable catalytic activity with high conversion and product selectivity in the ODH of EB to styrene with  $\text{CO}_2$  as the soft oxidant.

#### 4. Conclusions

In the present investigation, a 1:1 mole ratio  $\text{TiO}_2\text{-ZrO}_2$  mixed oxide support was prepared by a coprecipitation method and various active components namely, ceria, vanadia and ceria-vanadia were deposited by a wet impregnation method. The resulting samples calcined at  $550^\circ\text{C}$  exhibited high specific surface areas. In particular, the TZ support exhibited a high surface area of  $207\text{ m}^2/\text{g}$ . X-ray diffraction study of  $550^\circ\text{C}$  calcined samples revealed an amorphous nature of TZ support. With increase of calcination temperature ( $750^\circ\text{C}$ ), formation of crystalline  $\text{ZrTiO}_4$  compound was observed. In case of  $\text{V}_2\text{O}_5/\text{TZ}$  and  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TZ}$  samples, in addition to  $\text{ZrTiO}_4$  peaks, few other characteristic lines due to  $\text{ZrV}_2\text{O}_7$  and  $\text{CeVO}_4$  were observed. The XP spectra of V 2p revealed the existence of  $\text{V}^{4+}$  species at  $550^\circ\text{C}$  and  $\text{V}^{4+}$  species at

750 °C. The XPS profiles of Ce 3d indicated the presence of both  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  over the TZ support. However, Ti 2p and Zr 3d XPS bands revealed higher oxidation states (4+) for both Zr and Ti. Raman measurements further confirmed the formation of various compounds in the corresponding samples in agreement with XRD results. The TEM analysis suggested the presence of nanosized (<7 nm) particles with narrow range distribution. The TPR studies revealed that the reduction patterns of  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TZ}$  sample is a combination of the reduction profiles of  $\text{CeO}_2/\text{TZ}$  and  $\text{V}_2\text{O}_5/\text{TZ}$  samples with a low temperature shift suggesting the significant role of ceria addition. Among all the catalysts evaluated, the  $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TZ}$  combination sample exhibited highest conversion (56%) and product selectivity (98%). Contrarily, the  $\text{V}_2\text{O}_5/\text{TZ}$  sample showed a better activity in the first few hours and a faster deactivation was observed with time-on-stream owing to the coke formation. The remarkable ability of  $\text{CeO}_2$  in  $\text{V}_2\text{O}_5/\text{TZ}$  catalysts to achieve a high and stable activity is clearly apparent from the present study.

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